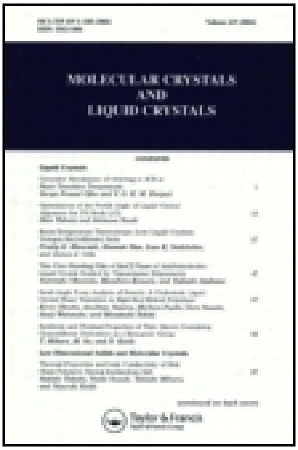

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PROTON SPIN–LATTICE RELAXATION DISPERSION STUDY OF THE FERROELECTRIC SMECTIC PHASES IN DOBAMBC

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Abstract The frequency dispersion of the proton spin–lattice relaxation rates T_1^{-1} in the ferroelectric smectic phases of DOBAMBC has been determined in the MHz region and analyzed in terms of the order fluctuations, self–diffusion, and rotational contributions to T_1^{-1}. In the smectic C* phase the main rate determining contribution are order fluctuations with a $T_1^{-1} \propto \nu_L^{-1/2}$ frequency dependence, whereas in the smectic H* phase the translational diffusion, which is slower than in the smectic C* phase, determines the dispersion of T_1^{-1}.

INTRODUCTION

In this paper the dispersion of the proton spin–lattice relaxation is used to study the molecular dynamics in the smectic C* and smectic H* phases of the chiral liquid crystal DOBAMBC (p–decyloxybenzylidene p′–amino 2–methyl butyl cinnamate). The characteristic feature of these two phases is the helicoidal structure in which the molecular director – tilted with respect to the smectic layers normal – precesses around this normal as one goes from one smectic layer to another. The pitch of the helix is of the order of one micron. When a single domain chiral smectic C* phase is formed by cooling from the isotropic and smectic A phase in a strong magnetic field, the axis of the helix orients parallel to the magnetic field[1,2]. The molecular director is tilted away by 10° – 25° [3]. The smectic C* and smectic H* phase differ, however, by the positional ordering of molecules within each smectic layer. The ordering is liquid-like in the smectic C* phase and crystal–like with a two–dimensional hexagonal lattice in the smectic H* phase. Local molecular rotations in these phases have been studied by ^{14}N nuclear quadrupole resonance[4] and by ^{13}C resonance spectroscopy[2]. It has been shown that fast biased hindered rotation of the rigid central part of the molecule occurs around the long molecular axis. As a consequence of the biasing, a net in–plane spontaneous polarization can be observed in both phases[5]. Additionally, orientational fluctuations of the central molecular part around the shorter axes take place. For DOBAMBC, in particular, the value of the corresponding "nematic" order parameter S varies between 0.8 and 0.9 in the Sm C* phase[2].

Up to date, nuclear spin–lattice relaxation processes have been carefully investigated in the smectic phases of a nonchiral liquid crystal (TBBA)[6-9]. Only recently a study of the temperature and angular dependences of the proton spin–lattice relaxation time in a chiral liquid crystal (DOBAMBC) has been done by Dong et al.[10]. In order to obtain quantitative information on the relaxation mechanisms in the ferroelectric smectic phases and on their characteristic parameters, we decided to study the dispersion of proton spin–lattice relaxation rate in the smectic C* and smectic H* phases of DOBAMBC, and to analyze it in terms of different relaxation mechanisms which can be involved.

EXPERIMENTAL

The proton spin relaxation dispersion, $T_1(\nu_L)$, was measured in the Larmor frequency range between 4 MHz and 270 MHz using the standard $\pi/2 - \tau - \pi/2$ pulse technique. The temperature dependences of the relaxation time in the laboratory frame (T_1) at two considerably different frequencies (90 MHz and 6.1 MHz), and of the relaxation time in the dipolar frame (T_{1D}) were determined as well. The experimental error was estimated to be smaller than $\pm$ 5 % for high and about $\pm$ 10 % for the low frequency regime. All measurements were performed on cooling the sample from the isotropic into the Sm A, Sm C*, Sm H*, and crystalline phase (I $\xrightarrow{117^\circ C}$ Sm A $\xrightarrow{93^\circ C}$ Sm C* $\xrightarrow{61^\circ C}$ Sm H* $\xrightarrow{51^\circ C}$ Cr). DOBAMBC, used in the experiment, had been synthesized in our laboratory[11].

The experimental results are presented in Figs. 1 and 2. The relaxation rate T_1^{-1} experiences both in the smectic C* (T = 76°C) and in the smectic H* ($T = 54^{o}$) phase a strong dispersion in the MHz frequency region (Fig. 1). A decrease in T_1^{-1} by a factor ~ 6 takes place over the range from ν_L = 4 MHz to 270 MHz. The shape of the T_1 dispersion definitely shows that it is of different type for the smectic C* and smectic H* phases. T_1^{-1} for the smectic H* phase is always higher than for smectic C* phase in the frequency range studied, and the ratio T_1^{-1} (Sm C*)/T_1^{-1} (Sm H*) depends on the frequency.

The temperature dependence of T_1, taken at 90 MHz and 6.1 MHz, shows – on going from the Sm C* to the Sm H* phase – only a small change in T_1, which hardly exceeds the experimental error (Fig. 2). A similar behaviour has been observed by Dong et al.[10] at 45 and 30 MHz. However, the relaxation time in the dipolar frame shows that in the kHz regime the two studied mesophases are separated by an abrupt change in the relaxation mechanisms.

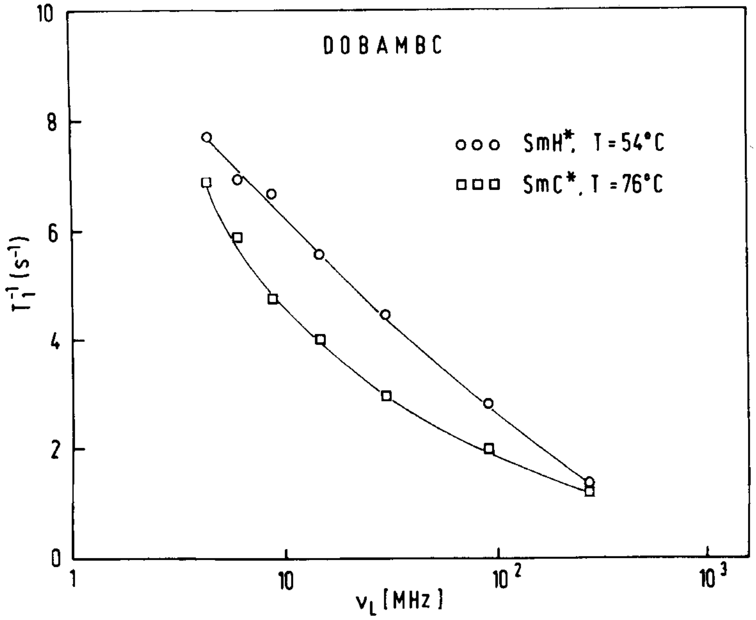

FIGURE 1. Comparison between the frequency dispersions of the proton spin–lattice relaxation rates in the smectic C* (T = 76°C) and in the smectic H* (T = 54°C) phase of DOBAMBC.

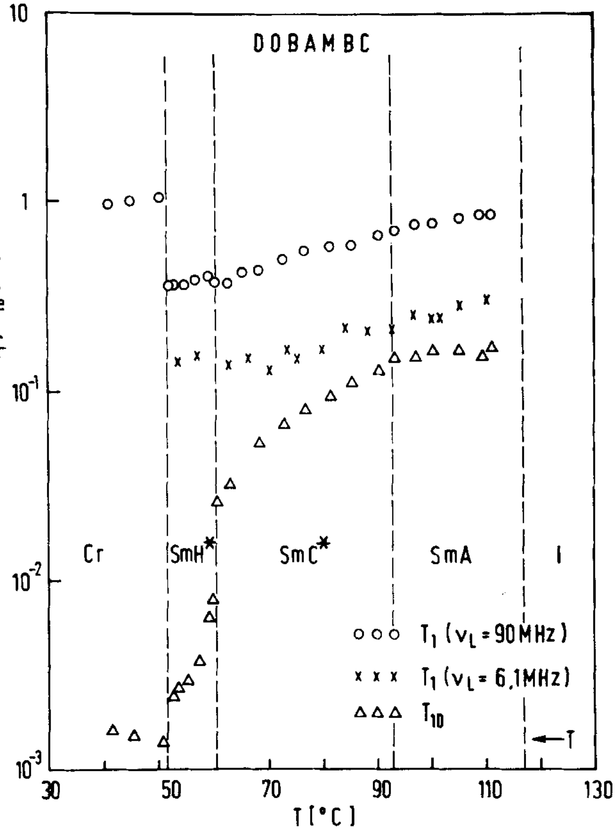

FIGURE 2. Temperature dependence of proton T_1 at 90 MHz and 6.1 MHz, and of T_{1D} in the smectic phases of DOBAMBC.

ANALYSIS AND DISCUSSION

In order to understand the origin of proton spin relaxation and, in particular, its dispersion behaviour one should take into account—in analogy with nematic liquid crystals[12]—several different relaxation mechanisms:

i) Order fluctuations contribute to the relaxation mainly by changing the orientation of the internuclear vector between two protons on the same molecule with respect to the external magnetic field. If certain conditions are met, the contribution of order fluctuations to the relaxation rate follows the characteristic frequency dependence:

$$(T_1^{-1})_{OF} = A \, . \, \nu_L^{-1/2} \quad . \tag{1}$$

The validity of this equation is restricted to the frequency region which is below the upper "cut–off" frequency determined by the dimension of the molecule, and above the lower "cut–off" determined by the fact that the wave length of order fluctuations cannot be larger than the dimension of the uniformly oriented domain or the dimension of the sample. A deviation from Eq.(1) at low frequencies can also be caused by the coupling of the nematic and smectic order fluctuations. In non–chiral smectic phases the contribution of order fluctuations has been detected in the smectic C phase at frequencies below 1 MHz [9], whereas the existence of relaxation induced by an order – fluctuations – like mechanism in the smectic phases with in-plane positional ordering is not clear [13].

ii) The contribution of molecular translational self–diffusion, $(T_1^{-1})_{SD}$, is caused by the modulation of the intermolecular dipolar interactions. The dependence of $(T_1^{-1})_{SD}$ on the Larmor frequency as predicted by the classical Torrey's theory [14] is strictly valid for isotropic liquids but useful, to a first approximation, also for the nematic [15], and smectic A and C phases [16]. The magnitude of $(T_1^{-1})_{SD}$ depends on ν_L, on the value of the self–diffusion constant D, and further on the distance of closest approach between two protons on neighbouring molecules a, on the spin density n, and slightly on the mean square length of the diffusion jump. The self–diffusion induced relaxation rate in the ordered smectic phases has been recently calculated by Žumer and Vilfan[13] and numerically evaluated for a series of parameters involved.

In the smectic phases with helicoidal structure the molecular diffusion along the helix modulates not only the intermolecular dipolar interactions as in spatially homogeneous systems but also the intramolecular dipolar coupling as the molecule slowly rotates when moving in the direction of the helix. This process, called "diffusion induced rotation", causes the relaxation rate $(T_1^{-1})_{DR}$, which exhibits the frequency dependence of the BPP type [17,18,19] with the correlation time τ_{DR} equal to:

$$\tau_{DR} = p^2/(16\,\pi^2\, D_h) \, . \tag{2}$$

Here p denotes the length of the pitch of the helix and D_h diffusion constant along the helix axis.

iii) The third contribution to the relaxation rate, $(T_1^{-1})_R$, is usually assumed to possess a Debye–like power spectrum as a first approximation to any type of local molecular reorientation, i.e. rotation around long and short molecular axes and deformations of the alkyl end chains. The relation

$$(T_1^{-1})_R = \frac{3}{10}\gamma^4\hbar^2 r^{-6}\epsilon\,[\tau_c/(1+\omega_L^2\tau_c^2) + 4\tau_c/(1+4\omega_L^2\tau_c^2)] \quad (3)$$

gives the relaxation rate due to rotation of spin pairs with r standing for the intramolecular interproton distance and τ_c for the rotation correlation time. ϵ is 1 for isotropic rotation, and smaller than 1 in anisotropic cases.

Smectic C* phase. In the smectic C* phase of DOBAMBC (at T = = 76°C) the experimentally determined frequency dependence of proton relaxation rate T_1^{-1} shows the presence of two different relaxation mechanisms (Fig. 3). The dominant contribution is frequency dependent and increases between 4 MHz and 90 MHz with decreasing frequency as $\nu_L^{-1/2}$ (Eq. 1) with deviations less than 10 %. The second contribution is nearly frequency independent in the investigated MHz region. Though our measurements do not cover such a wide frequency range as those made in the non–chiral liquid crystal TBBA[9], it seems reasonable enough to claim on the basis of the above fact that the dominant, frequency dependent relaxation mechanism between 1 and 100 MHz in the smectic C* phase of DOBAMBC are order fluctuations. From the experimental data we find the value of the constant A, which indicates the "strength" of order fluctuations mechanism, to be $(12.5 \pm 0.3) \cdot 10^3\ s^{-3/2}$. It is considerably larger than in the smectic C phase of the non–chiral TBBA[9] indicating a stronger role of order fluctuations in the case of DOBAMBC. It should be mentioned that the constant A used for the smectic C* phase presents in fact the weighted sum of constants A for the contributions of spectral densities at ω_L and at $2\omega_L$ – in the nematic case only the spectral density at ω_L is different from zero – what is a consequence of the tilt of the molecules with respect to the magnetic field and possibly uncomplete orientation of the sample. The contribution $(T_1^{-1})_{OF}$ exhibits no deviation from the $(T_1^{-1})_{OF} \propto \nu_L^{-1/2}$ behaviour at the upper end of the frequency range investigated. Therefore, the upper "cut–off" frequency in the smectic C* phase of DOBAMBC should be > 100 MHz in contrast to $\nu_{c,max}$ in TBBA which has been determined to be only $2 \cdot 10^5$ Hz[9]. The reason for this difference is not yet clear.

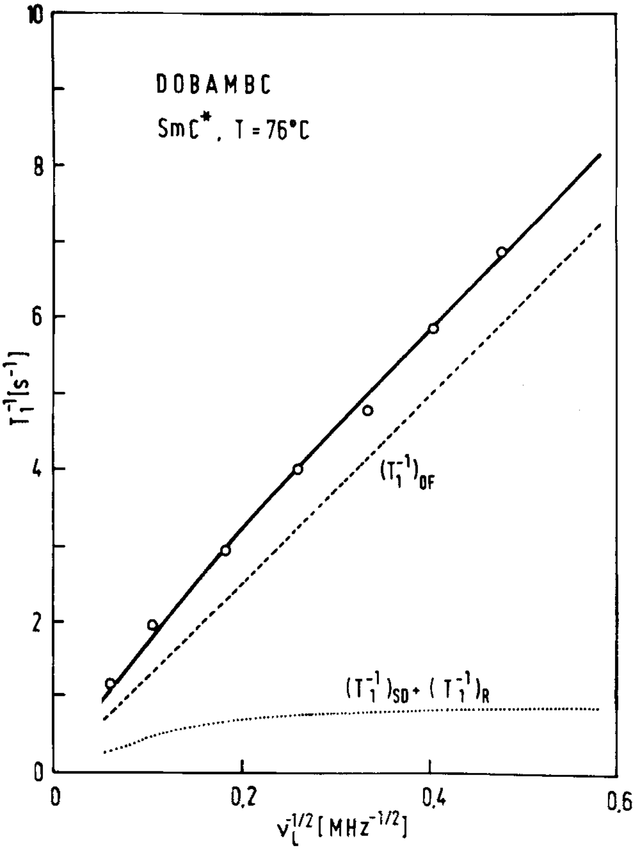

FIGURE 3. Frequency dispersion of the proton spin–lattice relaxation rate T_1^{-1} in the smectic C* phase of DOBAMBC at 76°C. The solid line represents the sum of computer fitted order fluctuation $(T_1^{-1})_{OF}$, self–diffusion $(T_1^{-1})_{SD}$, and rotation $(T_1^{-1})_R$ contributions to the experimental data, which are denoted by circles.

The second, nearly frequency independent contribution to the total relaxation rate can be ascribed either to the modulation of the intermolecular dipolar interactions by translational self–diffusion $(T_1^{-1})_{SD}$, to fast local molecular rotation $(T_1^{-1})_R$, or to a combination of both of them. In the case that it is interpreted in terms of $(T_1^{-1})_{SD}$ only – calculated for simplicity according to Torrey's formula[14] reduced by the factor 1.4[15] – fits to the experimental data can be obtained for all values of the diffusion constant ranging from $D = 1.5 \cdot 10^{-10}$ m^2/s to $D = 1.1 \cdot 10^{-10}$ m^2/s with the corresponding a increasing from 3 Å to 4 Å. On the other hand, the fitting of the calculated $(T_1^{-1})_R$ (Eq. 3) to the experimentally determined frequency nearly independent contribution yields the correlation time for local molecular rotation τ_c equal to $3 \cdot 10^{-10}$ s and $\epsilon = 0.11$ if r (ring protons) = 2.44 Å and r (alkyl protons) = 1.79 Å. In both cases, i.e. in the interpretation of the second contribution to T_1^{-1} by $(T_1^{-1})_{SD}$ only and by $(T_1^{-1})_R$ only, the values of the parameters which provide a good fit are some what dubious. The diffusion constant $D = 1.1 \cdot 10^{-10}$ m^2/s is about 50 percents larger than expected on the basis of the preliminary direct NMR measurements of diffusion constant in the smectic C* phase of DOBAMBC[20]. Also the value of the correlation time τ_c exceeds for more than an order of magnitude the value determined for the smectic C phase of TBBA by neutron scattering[21]. Therefore we think that the second contribution to T_1^{-1} in the smectic C* phase of DOBAMBC results from a combined effect of translational self-diffusion modulating intermolecular dipolar interactions, and local rotations modulating intramolecular interactions. The characteristic parameters for these two motions can not be uniquely determined from our data in view of the relatively small and frequency nearly independent contribution they yield to the total relaxation rate. The dotted line in Fig. 3 is plotted for example for $D = 9 . 10^{-11}$ m^2/s, a = 5 Å, $(T_1^{-1})_R$ = 0.2 s^{-1}, and using n = 0.05 Å^{-3} and relation $\langle r^2 \rangle \sim a^2$ for the mean square diffusion jump distance, but this is not the only set of parameters which fits the experimental data.

Smectic H* phase. The smectic H* phase of DOBAMBC exhibits at T = 54°C a completely different proton relaxation dispersion behaviour to that observed earlier in TBBA[8]. The experimental data do not follow the Debye—like relaxation characteristic for the local molecular reorientation of any type and for the translational diffusion induced relaxation in the region with $\omega_L \tau_{D\perp} \gg 1$, where $\tau_{D\perp}$ denotes the average time between two successive diffusion jumps in the smectic layer. They can be described, however, by the $(T_1^{-1})_{SD}$ relaxation mechanism in the regime with $\omega_L \tau_{D\perp} < 1$ plus a small frequency independent contribution which can be ascribed to fast local molecular rotation, $(T_1^{-1})_R$ (Fig. 4).

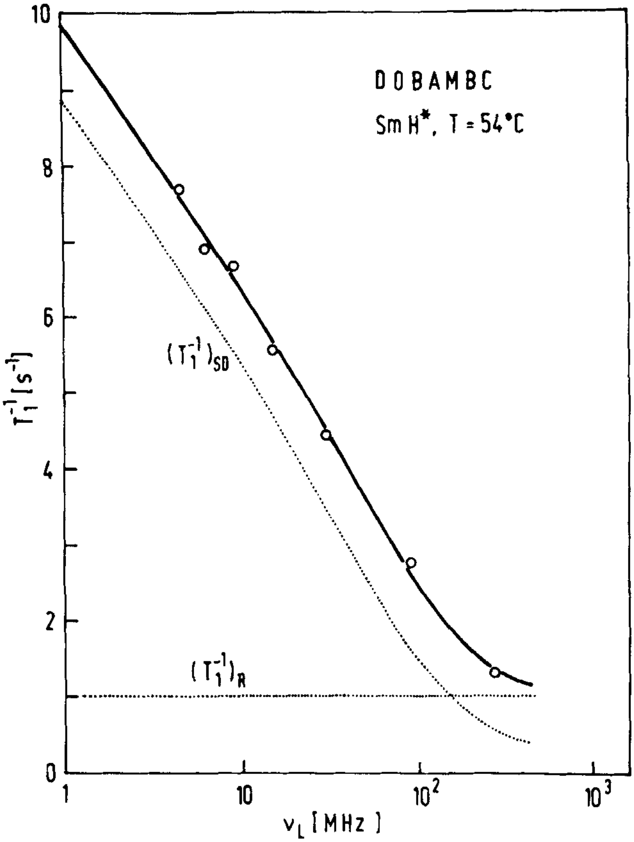

FIGURE 4. Frequency dispersion of the proton spin—lattice relaxation rate T_1^{-1} in the smectic H* phase of DOBAMBC at 54°C. The solid line represents the sum of computer fitted self—diffusion $(T_1^{-1})_{SD}$ and rotation $(T_1^{-1})_R$ contributions to the experimental data (denoted by circles).

The calculated $(T_1^{-1})_{SD}$ curve in Fig. 4 represents the contribution of translational self–diffusion in ordered smectic phases as given in Ref. (13) (the case which implies the anisotropy of the diffusion constants in the layer plane $D_\perp$ and in the perpendicular .direction $D_\parallel$ equal to $D_\perp/D_\parallel = 2$, uniform spin distribution of spins along the molecule, $n = 0.05$ Å^{-3}, molecular shape anisotropy $\ell/d \sim 5$, and polycrystalline sample). The parameters which are more relevant for the dispersion behaviour and magnitude of $(T_1^{-1})_{SD}$ and which were determined by fitting the experimental data of DOBAMBC at T = 54°C are: $\tau_{D\perp} = 1.8 \cdot 10^{-9}$ s, molecular diameter d = 4 Å, and $(T_1^{-1})_R = 1\ s^{-1}$. From $\tau_{D\perp}$ and d the value of the in–plane self–diffusion constant $D_\perp$ can be calculated. The relation $D_\perp = d^2/(4\tau_{D\perp})$ yields $D_\perp \cong 2 \cdot 10^{-11}\ m^2/s$. The fitted value of $D_\perp$ in the smectic H* phase of DOBAMBC is thus surprisingly large for an ordered smectic phase, though a similar value $D_\perp = 1.2 \cdot 10^{-11}\ m^2/s$ has been already reported for IBPBAC[22].

It can be mentioned that the frequency dispersion of experimental T_1^{-1} in the smectic H* phase can be formally — though with a larger mean square deviation — simulated also by the dispersion of $(T_1^{-1})_{OF}$ if the effect of the lower "cut–off" frequency $\nu_{c,min}$ is included in Eq. (1)[23] with $\nu_{c,min} = 12$ MHz, but it is hard to expect that an order—fluctuations—like relaxation mechanism would be important in an ordered smectic phase.

In conclusion we may say that the observed frequency dependences of the proton spin–lattice relaxation rate in the ferroelectric phases of DOBAMBC in the MHz region indicate order fluctuations to be the main relaxation mechanism in the smectic C* phase, and translational diffusion to dominate the relaxation process in the smectic H* phase. In view of the large difference between T_1 and T_{1D} in the smectic H* phase, an additional relaxation mechanism important only at very low frequencies, is expected to exist. This is probably "diffusion induced rotation" whose characteristic correlation time τ_{DR} is of the order $10^{-4} - 10^{-5}$ s in DOBAMBC. It could be investigated by an extension of the dispersion study to the frequencies in the kHz regime.

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